

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 June 2001 (07.06.2001)

PCT

(10) International Publication Number
WO 01/39735 A1

- (51) International Patent Classification⁷: **A61K 7/06**
- (21) International Application Number: **PCT/US99/28511**
- (22) International Filing Date: 2 December 1999 (02.12.1999)
- (25) Filing Language: English
- (26) Publication Language: English
- (71) Applicant (for all designated States except US): **THE PROCTER & GAMBLE COMPANY** [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **VENKATESWARAN, Ananthanarayan** [IN/JP]; 1-4-127-904, Koyo-cho Naka, Higashinada-ku, Kobe 658-0032 (JP). **NAKAMURA, Kiichiro** [JP/JP]; 1-10-101-3702, Koyo-cho Naka, Higashinada-ku, Kobe 658-0032 (JP). **SCOTT, Louise, Gail** [GB/JP]; 1-14-11, Sumiyoshi Honmachi, Higashinada-ku, Kobe 658-0051 (JP). **OHTSU, Kumiko** [JP/JP]; Cassita Okamoto #104, 6-4-18, Motoyamakitamchi, Higashinada-ku, Kobe 658-0003 (JP).
- (74) Agents: **REED, T., David et al.**; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217-1087 (US).
- (81) Designated States (national): AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GE, GM, GR, GU, HK, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **CONDITIONING SHAMPOO COMPOSITIONS**

(57) **Abstract:** Disclosed is a conditioning shampoo composition comprising by weight: (a) from about 0.05 % to about 50 % of an anionic surfactant wherein the anionic surfactant is substantially a monohydric anionic surfactant; (b) from about 0.05 % to about 20 % of a cationic silicone emulsion comprising, by weight of the cationic silicone emulsion, from about 2 % to about 20 % of a cationic surfactant; and an emulsifiable amount of a mechanically emulsified silicone compound having a particle size of from about 0.2 microns to about 2.5 microns; and (c) an aqueous carrier; wherein a colloidal coacervate is made by diluting the composition with water by about 10 folds, the colloidal coacervate having an average particle size of less than about 30 microns.

WO 01/39735 A1

CONDITIONING SHAMPOO COMPOSITIONS

5

10

TECHNICAL FIELD

The present invention relates to conditioning shampoo compositions comprising a cationic silicone emulsion.

BACKGROUND

15

Human hair becomes soiled due to its contact with the surrounding environment and from the sebum secreted by the scalp. The soiling of hair causes it to have a dirty feel and an unattractive appearance. The soiling of the hair necessitates shampooing with frequent regularity.

20

Shampooing cleans the hair by removing excess soil and sebum. However, shampooing can leave the hair in a wet, tangled, and generally unmanageable state. Once the hair dries, it is often left in a dry, rough, lusterless, or frizzy condition due to removal of the hair's natural oils and other natural conditioning and moisturizing components. The hair can further be left with increased levels of static upon drying, which can interfere with combing and result in a condition commonly referred to as "fly-away hair", or contribute to an undesirable phenomena of "split ends", particularly for long hair.

25

A variety of approaches have been developed to alleviate these after-shampoo problems. These approaches range from post-shampoo application of hair conditioners such as leave-on and rinse-off products, to hair conditioning shampoos which attempt to both clean and condition the hair from a single product.

30

Cationic conditioning materials are useful in conditioning shampoos due to their conditioning benefits when the hair is dried. Coacervate formation in a shampoo composition is known to be advantageous for incorporating cationic conditioning agents to provide a stable product. The use of cationic conditioning

35

agents to form coacervates are known in the art, such as in PCT publications WO93/08787, WO95/01152, and JP Kokai H10-175827.

Generally, conditioning shampoo compositions which provide benefits described above are also known to weigh down hair or provide hair volume-down. For consumers who desire hair volume-up such as consumers having fine hair, the effect of hair volume-down is not desirable. The term "hair volume-up" as used herein is not equal to fly-away hair. Fly-away hair is due to the increased level of static, and represents volume increase of only very minor amount of the hair as a whole, and is not desirable. On the other hand, hair volume-up as used herein relates to increase of the bulk of the hair volume. Consumers having fine hair have the desire to achieve hair volume-up while controlling undesirable fly-away of the hair.

Based on the foregoing, there remains a desire to provide conditioning shampoo compositions which provide hair volume-up while not compromising conditioning benefits such as manageability, and ease to comb, and fly-away control.

None of the existing art provides all of the advantages and benefits of the present invention.

20

SUMMARY

The present invention is directed to a conditioning shampoo composition comprising by weight:

- (a) from about 0.05% to about 50% of an anionic surfactant wherein the anionic surfactant is substantially a monohydric anionic surfactant;
- 25 (b) from about 0.05% to about 20% of a cationic silicone emulsion comprising, by weight of the cationic silicone emulsion, from about 2% to about 20% of a cationic surfactant; and an emulsifiable amount of a mechanically emulsified silicone compound having a particle size of from about 0.2 microns to about 2.5 microns; and
- 30 (c) an aqueous carrier;

wherein a colloidal coacervate is made by diluting the composition with water by about 10 folds, the colloidal coacervate having an average particle size of less than about 30 microns.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION

While the specification concludes with claims which particularly point out and distinctly claim the invention, it is believed the present invention will be better understood from the following description.

All cited references are incorporated herein by reference in their entireties.

Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

Herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

All percentages, parts and ratios are based upon the total weight of the compositions of the present invention, unless otherwise specified. All such weights as they pertain to listed ingredients are based on the active level and, therefore, do not include carriers or by-products that may be included in commercially available materials.

MONOHYDROPHILIC ANIONIC SURFACTANT

The present invention comprises by weight from about 0.05% to about 50%, preferably from about 0.1% to about 30%, more preferably from about 0.5% to about 20% of an anionic surfactant wherein the anionic surfactant is substantially a monohydric anionic surfactant. Monohydrophilic anionic surfactants useful herein are those having just one anionic hydrophilic group in the molecule. Preferably, the hydrophilic group is selected from the group consisting of carboxy, sulfate, sulfonate, and phosphate groups, more preferably a sulfate.

Monohydrophilic anionic surfactants useful herein include alkyl and alkyl ether sulfates. These materials have the respective formulae ROSO_3M and $\text{RO}(\text{C}_2\text{H}_4\text{O})_x\text{SO}_3\text{M}$, wherein R is alkyl or alkenyl of from about 8 to about 30 carbon atoms, x is 1 to about 10, and M is hydrogen or a cation such as ammonium, alkanolammonium (e.g., triethanolammonium), a monovalent metal cation (e.g., sodium and potassium), or a polyvalent metal cation (e.g., magnesium and calcium). Preferably, M should be chosen such that the

monohydrophilic anionic surfactant component is water soluble. The monohydrophilic anionic surfactant or surfactants should be chosen such that the Krafft temperature is about 15°C or less, preferably about 10°C or less, and more preferably about 0°C or less. It is also preferred that the monohydrophilic anionic surfactant be soluble in the composition hereof.

Krafft temperature refers to the point at which solubility of an ionic surfactant becomes determined by crystal lattice energy and heat of hydration, and corresponds to a point at which solubility undergoes a sharp, discontinuous increase with increasing temperature. Each type of surfactant will have its own characteristic Krafft temperature. Krafft temperature for ionic surfactants is, in general, well known and understood in the art. See, for example, Myers, Drew, Surfactant Science and Technology, pp. 82-85, VCH Publishers, Inc. (New York, New York, USA), 1988 (ISBN 0-89573-399-0), which is incorporated by reference herein in its entirety.

In the alkyl and alkyl ether sulfates described above, preferably R has from about 12 to about 18 carbon atoms in both the alkyl and alkyl ether sulfates. The alkyl ether sulfates are typically made as condensation products of ethylene oxide and monohydric alcohols having from about 8 to about 24 carbon atoms. The alcohols can be derived from fats, e.g., coconut oil, palm oil, tallow, or the like, or the alcohols can be synthetic. Lauryl alcohol and straight chain alcohols derived from coconut oil and palm oil are preferred herein. Such alcohols are reacted with 1 to about 10, and especially about 3, molar proportions of ethylene oxide and the resulting mixture of molecular species having, for example, an average of 3 moles of ethylene oxide per mole of alcohol, is sulfated and neutralized.

Specific examples of alkyl ether sulfates which can be used in the present invention are sodium and ammonium salts of coconut alkyl triethylene glycol ether sulfate; tallow alkyl triethylene glycol ether sulfate, and tallow alkyl hexaoxyethylene sulfate. Highly preferred alkyl ether sulfates are those comprising a mixture of individual compounds, said mixture having an average alkyl chain length of from about 12 to about 16 carbon atoms and an average degree of ethoxylation of from 1 to about 4 moles of ethylene oxide. Such a mixture also comprises from 0% to about 20% by weight C₁₂₋₁₃ compounds; from about 60% to about 100% by weight of C₁₄₋₁₅₋₁₆ compounds, from 0% to about 20% by weight of C₁₇₋₁₈₋₁₉ compounds; from about 3% to about 30% by

weight of compounds having a degree of ethoxylation of 0; from about 45% to about 90% by weight of compounds having a degree of ethoxylation of from 1 to about 4; from about 10% to about 25% by weight of compounds having a degree of ethoxylation of from about 4 to about 8; and from about 0.1% to about 15% by weight of compounds having a degree of ethoxylation greater than about 8.

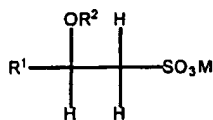
Other suitable monohydrophilic anionic surfactants are the water-soluble salts of organic, sulfuric acid reaction products of the general formula $[R^1-SO_3-M]$ where R^1 is selected from the group consisting of a straight or branched chain, saturated aliphatic hydrocarbon radical having from about 8 to about 24, preferably about 10 to about 18, carbon atoms; and M is as previously described above in this section. Examples of such surfactants are the salts of an organic sulfuric acid reaction product of a hydrocarbon of the methane series, including iso-, neo-, and n-paraffins, having about 8 to about 24 carbon atoms, preferably about 12 to about 18 carbon atoms and a sulfonating agent, e.g., SO_3 , H_2SO_4 , obtained according to known sulfonation methods, including bleaching and hydrolysis. Preferred are alkali metal and ammonium sulfonated C_{10-18} n-paraffins.

Other monohydrophilic anionic surfactants include olefin sulfonates having about 10 to about 24 carbon atoms. The term "olefin sulfonates" is used herein to mean compounds which can be produced by the sulfonation of alpha-olefins by means of uncomplexed sulfur trioxide, followed by neutralization of the acid reaction mixture in conditions such that any sulfones which have been formed in the reaction are hydrolyzed to give the corresponding hydroxy-alkanesulfonates. The sulfur trioxide can be liquid or gaseous, and is usually, but not necessarily, diluted by inert diluents, for example by liquid SO_2 , chlorinated hydrocarbons, etc., when used in the liquid form, or by air, nitrogen, gaseous SO_2 , etc., when used in the gaseous form. The α -olefins from which the olefin sulfonates are derived are mono-olefins having about 12 to about 24 carbon atoms, preferably about 14 to about 16 carbon atoms. Preferably, they are straight chain olefins. In addition to the true alkene sulfonates and a proportion of hydroxy-alkanesulfonates, the olefin sulfonates can contain minor amounts of other materials, such as alkene disulfonates depending upon the reaction conditions, proportion of reactants, the nature of the starting olefins and impurities in the olefin stock and side reactions during the sulfonation process. A specific α -olefin sulfonate mixture of the above type is described more fully in

U.S. Patent 3,332,880, to Pflaumer and Kessler, issued July 25, 1967, which is incorporated by reference herein in its entirety.

Still other suitable monohydrophilic anionic surfactants are the reaction products of fatty acids esterified with isethionic acid and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut or palm oil; or sodium or potassium salts of fatty acid amides of methyl tauride in which the fatty acids, for example, are derived from coconut oil. Other similar monohydrophilic anionic surfactants are described in U.S. Patents 2,486,921, 2,486,922, and 2,396,278, which are incorporated by reference herein in their entirety.

Another class of monohydrophilic anionic surfactants suitable for use in the shampoo compositions are the β -alkyloxy alkane sulfonates. These compounds have the following formula:



15

where R^1 is a straight chain alkyl group having from about 6 to about 20 carbon atoms, R^2 is a lower alkyl group having from about 1, preferred, to about 3 carbon atoms, and M is as hereinbefore described. Many other monohydrophilic anionic surfactants suitable for use in the shampoo compositions are described in McCutcheon's, Emulsifiers and Detergents, 1989 Annual, published by M. C. Publishing Co., and in U.S. Patent 3,929,678, which descriptions are incorporated herein by reference in their entirety.

Another class of suitable monohydrophilic anionic surfactants are amino acid surfactants which are surfactants that have the basic chemical structure of an amino acid compound, i.e., that contains a structural component of one of the naturally-occurring amino acids.

Preferred monohydrophilic anionic surfactants for use in the shampoo compositions include ammonium laureth sulfate, triethylamine laureth sulfate, triethanolamine laureth sulfate, monoethanolamine laureth sulfate, diethanolamine laureth sulfate, lauric monoglyceride sodium sulfate, sodium laureth sulfate, potassium laureth sulfate, sodium tridecyl benzene sulfonate, sodium dodecyl benzene sulfonate, N-cocoylalaninate, N-acyl-N-methyl- β -alaninate, sodium laurylsarcosinate, cocoyl sarcosine, lauroyl taurate, lauroyl

30

lactylate, N-acyl potassium glycine, lauroamphohydroxy propylsulfonate, cocoglyceride sulfate, lauroyl isethionate, lauroamphoacetate, and mixtures thereof.

CATIONIC SILICONE EMULSION

5 The conditioning shampoo composition of the present invention comprises a cationic silicone emulsion. The cationic silicone emulsion herein is a pre-dispersed stable emulsion comprising at least a cationic surfactant, a silicone compound, and water.

10 The cationic silicone emulsion herein, together with the monohydrophilic anionic surfactant is believed to provide increase in bulk hair volume while not deteriorating conditioning benefits such as fly-away control. It is of particular significance that, in the present invention the cationic surfactant is present in the silicone emulsion, and not just in the bulk of the composition. Cationic surfactant is typically included in the bulk of a conditioning shampoo composition for hair
15 conditioning benefits such as fly-away control, however does not contribute to increase of hair volume. It has been surprisingly found that when cationic surfactant is included in the silicone emulsion, increase in bulk hair volume is significantly improved than when the same amount of cationic surfactant is included in the bulk of the composition, and at the same time provides good
20 conditioning benefits.

 When the present composition is diluted, the cationic silicone emulsion and the monohydrophilic anionic surfactant form a characteristic colloidal and discrete coacervate which precipitates from the bulk of the composition. The coacervates obtained by dilution of the present invention is in the form of discrete
25 crystals having an average particle size of less than about about 30 microns, preferably less than about 20 microns when measured by microscope. Without being bound by theory, it is believed that such small size coacervates, when deposited on hair, change the fiber-fiber orientation and therefore the spatial interaction of the hair, resulting in increased hair volume. The coacervate can be
30 observed by diluting the present composition by about 2-50 folds, typically about 10 folds, and immediately obtaining a sample from the dilution.

 The cationic silicone emulsion comprises, by weight of the cationic silicone emulsion, from about 1% to about 20%, preferably from about 2% to about 8%, of a cationic surfactant; and an emulsifiable amount of silicone compound. The
35 silicone compound is preferably comprised from about 0.1% to about 70%, more

preferably from about 5% to about 60% by weight of the cationic silicone emulsion.

The cationic silicone emulsion is included in the composition at a level by weight from about 0.1% to about 20%, more preferably from about 0.5% to about 5%.

The cationic silicone emulsion can be made by any convenient method known in the art, preferably by mechanical emulsification.

For example, the cationic silicone emulsion may be made by mechanical emulsification by taking a polysiloxane polymer and emulsifying it in water in the presence of at least one emulsifying agent using mechanical means such as agitation, shaking and homogenization. The emulsifying agent can be the cationic surfactant comprised in the cationic silicone emulsion, or other suitable surfactant. Mechanical emulsification may require use of two or more surfactants, and two or more mixing processes using different surfactants. Two or more types of silicone compounds, such as a highly viscous silicone compound and a low viscosity silicone compound, may be used. One particularly preferred process for obtaining the cationic silicone emulsion of the present invention via mechanical emulsification is through the process disclosed in EP Publication 460,683A, which is incorporated herein by reference in its entirety. In this reference, it is disclosed that the emulsion is prepared by combining the polysiloxane, water, and a primary nonionic surfactant having an HLB value of 15-19 to form a first mixture, adding to the first mixture a co-surfactant selected from the group consisting of nonionic, cationic and anionic surfactants having an HLB value of 1.8-15 to form a second mixture and mixing the second mixture at a temperature of about 40°C, until the particle size of the polysiloxane in the emulsion is less than about three hundred nanometers.

The cationic silicone emulsion herein may be made by emulsion polymerization. An emulsion polymerization process includes taking a polysiloxane monomer and/or oligomer and emulsifying it in water in the presence of a catalyst to form the polysiloxane polymer. It is understood that unreacted monomers and oligomers may remain in an emulsion polymerized silicone emulsion. One particularly preferred process for obtaining the cationic silicone emulsion of the present invention via emulsion polymerization is through the process disclosed in GB application 2,303,857, which is incorporated herein by reference in its entirety. This reference discloses a process for making stable

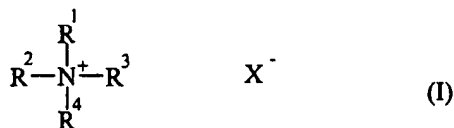
cationic silicone oil-in-water emulsion comprising: 1) blending a mixture of silicones selected from the group consisting of cyclic silicone oligomers, mixed silicone hydrolyzates, silanol stopped oligomers, high molecular weight silicone polymers, and functionalized silicones with 2) water, and 3) an anionic surfactant; 4) heating the blend to a temperature ranging from about 75 to about 98°C for a period of time ranging from about 1 hours to about 5 hours; 5) cooling the heated blend to a temperature ranging from 0 to about 25°C for a period of time ranging from about 3 hours to about 24 hours; 6) adding a compatibilizing surfactant selected from the group consisting of nonionic surfactant having an HLB ratio greater than 9; and 7) adding a cationic surfactant.

The silicone compound in the cationic silicone emulsion has a particle size of from about 0.2 to about 2.5 microns, preferably from about 0.2 to about 0.5 microns. The particle size of the silicone compound is believed to affect the deposition of the silicone compound on the hair. The particle size of the silicone compound is determined based on the desired deposition and uniformity of distribution of the silicone compound.

Cationic Surfactant

The cationic silicone emulsion herein comprises a cationic surfactant. The cationic surfactant useful herein is any known to the artisan, and is preferably included in the cationic silicone emulsion at a level by weight from about 1% to about 20%, more preferably from about 2% to about 8%.

Among the cationic surfactants useful herein are those corresponding to the general formula (I):



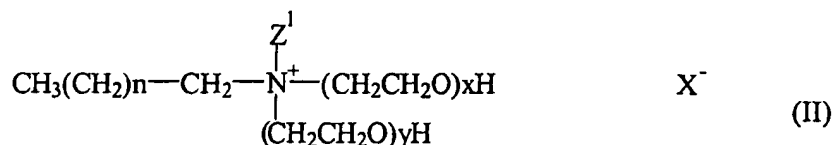
wherein at least one of R¹, R², R³, and R⁴ is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of R¹, R², R³, and R⁴ are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate,

phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or
5 unsaturated. Preferred is when R¹, R², R³, and R⁴ are independently selected from C₁ to about C₂₂ alkyl. Nonlimiting examples of cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-8, quaternium-14, quaternium-18, quaternium-18 methosulfate, quaternium-24, and mixtures thereof.

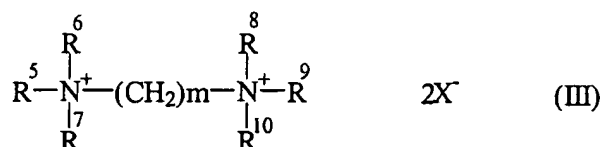
10 Among the cationic surfactants of general formula (I), preferred are those containing in the molecule at least one alkyl chain having at least 16 carbons. Nonlimiting examples of such preferred cationic surfactants include: behenyl trimethyl ammonium chloride available, for example, with tradename INCROQUAT TMC-80 from Croda and ECONOL TM22 from Sanyo Kasei; cetyl
15 trimethyl ammonium chloride available, for example, with tradename CA-2350 from Nikko Chemicals, hydrogenated tallow alkyl trimethyl ammonium chloride, dialkyl (14-18) dimethyl ammonium chloride, ditallow alkyl dimethyl ammonium chloride, dihydrogenated tallow alkyl dimethyl ammonium chloride, distearyl dimethyl ammonium chloride, dicetyl dimethyl ammonium chloride,
20 di(behenyl/arachidyl) dimethyl ammonium chloride, dibehenyl dimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride, stearyl propyleneglycol phosphate dimethyl ammonium chloride, stearyl amidopropyl dimethyl benzyl ammonium chloride, stearyl amidopropyl dimethyl (myristylacetate) ammonium chloride, and N-(stearyl colamino formyl methy)
25 pyridinium chloride.

Also preferred are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the R¹ - R⁴ radicals contain one or more
30 hydrophilic moieties selected from alkoxy (preferably C₁ - C₃ alkoxy), polyoxyalkylene (preferably C₁ - C₃ polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic conditioning surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. Preferred hydrophilically

substituted cationic surfactants include those of the formula (II) through (VIII) below:



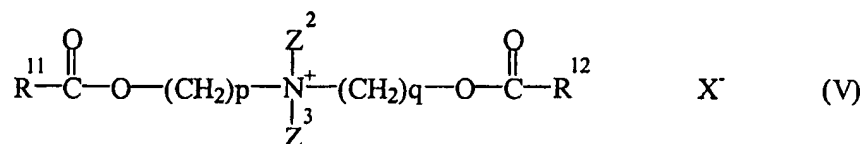
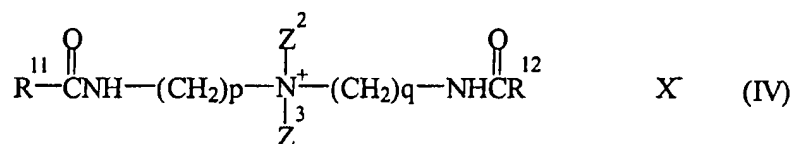
- 5 wherein n is from 8 to about 28, x+y is from 2 to about 40, Z¹ is a short chain alkyl, preferably a C₁ - C₃ alkyl, more preferably methyl, or (CH₂CH₂O)_zH wherein x+y+z is up to 60, and X is a salt forming anion as defined above;



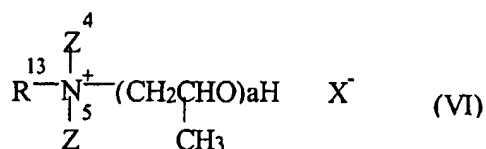
10

wherein m is 1 to 5, one or more of R⁵, R⁶, and R⁷ are independently an C₁ - C₃₀ alkyl, the remainder are CH₂CH₂OH, one or two of R⁸, R⁹, and R¹⁰ are independently an C₁ - C₃₀ alkyl, and remainder are CH₂CH₂OH, and X is a salt forming anion as mentioned above;

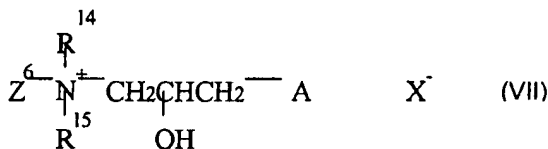
15



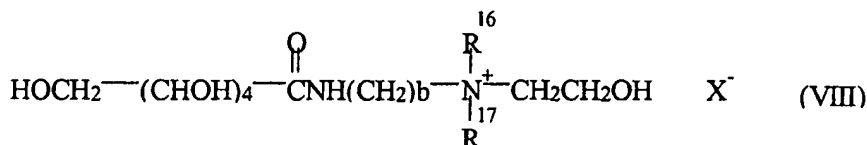
- 20 wherein, independently for formulae (IV) and (V), Z² is an alkyl, preferably a C₁ - C₃ alkyl, more preferably methyl, and Z³ is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl, p and q independently are integers from 2 to 4, inclusive, preferably from 2 to 3, inclusive, more preferably 2, R¹¹ and R¹², independently, are substituted or unsubstituted hydrocarbyls, preferably C₁₂ -
25 C₂₀ alkyl or alkenyl, and X is a salt forming anion as defined above;



- wherein R¹³ is a hydrocarbyl, preferably a C₁ - C₃ alkyl, more preferably methyl, Z⁴ and Z⁵ are, independently, short chain hydrocarbyls, preferably C₂ - C₄ alkyl or alkenyl, more preferably ethyl, a is from 2 to about 40, preferably from about 7 to about 30, and X is a salt forming anion as defined above;



- wherein R¹⁴ and R¹⁵, independently, are C₁ - C₃ alkyl, preferably methyl, Z⁶ is a C₁₂ - C₂₂ hydrocarbyl, alkyl carboxy or alkylamido, and A is a protein, preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or hydrolyzed forms thereof; and X is a salt forming anion as defined above;



- wherein b is 2 or 3, R¹⁶ and R¹⁷, independently are C₁ - C₃ hydrocarbyls preferably methyl, and X is a salt forming anion as defined above. Nonlimiting examples of hydrophilically substituted cationic surfactants useful in the present invention include the materials having the following CTFA designations: quaternium-16, quaternium-26, quaternium-27, quaternium-30, quaternium-33, quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-61, quaternium-62, quaternium-70, quaternium-71, quaternium-72, quaternium-75, quaternium-76 hydrolyzed collagen, quaternium-77, quaternium-78, quaternium-79 hydrolyzed collagen, quaternium-79 hydrolyzed keratin, quaternium-79 hydrolyzed milk protein, quaternium-79 hydrolyzed silk, quaternium-79 hydrolyzed soy protein, and quaternium-79 hydrolyzed wheat protein, quaternium-80, quaternium-81, quaternium-82, quaternium-83, quaternium-84, and mixtures thereof.

Highly preferred hydrophilically substituted cationic surfactants include dialkylamido ethyl hydroxyethylmonium salt, dialkylamidoethyl dimonium salt, dialkyloyl ethyl hydroxyethylmonium salt, dialkyloyl ethyldimonium salt, and mixtures thereof; for example, commercially available under the following tradenames; VARISOFT 110, VARIQUAT K1215 and 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25, ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODUOQUAD from Akzo, DEHYQUAT SP from Henkel, and ATLAS G265 from ICI Americas.

Salts of primary, secondary, and tertiary fatty amines are also suitable cationic surfactants. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and can be substituted or unsubstituted. Particularly useful are amidoamines of the following general formula:



wherein R^1 is a residue of C_{11} to C_{24} fatty acids, R^2 is a C_1 to C_4 alkyl, and m is an integer from 1 to 4.

Preferred amidoamine useful in the present invention includes stearamidopropyldimethylamine, stearamidopropyldiethylamine, stearamidoethyldiethylamine, stearamidoethyldimethylamine, palmitamidopropyldimethylamine, palmitamidopropyldiethylamine, palmitamidoethyldiethylamine, palmitamidoethyldimethylamine, behenamidopropyldimethylamine, behenamidopropyldiethylamine, behenamidoethyldiethylamine, behenamidoethyldimethylamine, arachidamidopropyldimethylamine, arachidamidopropyldiethylamine, arachidamidoethyldiethylamine, arachidamidoethyldimethylamine, and mixtures thereof; more preferably stearamidopropyldimethylamine, stearamidoethyldiethylamine, and mixtures thereof.

The amidoamines herein are preferably partially quaternized with the acids selected from the group consisting of L-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, L-glutamic acid hydrochloride, tartaric acid, and mixtures thereof; preferably L-glutamic acid, lactic acid, hydrochloric acid, and mixtures thereof.

Preferably, the mole ratio of amidoamine to acid is from about 1:0.3 to about 1:1, more preferably from about 1:0.5 to about 1:0.9.

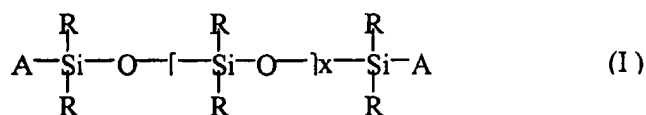
Silicone Compound

The cationic silicone emulsion herein comprises a silicone compound in an amount capable of providing a stable emulsion, preferably from about 0.1% to about 70%, more preferably from about 5% to about 60% by weight of the cationic silicone emulsion. The amount of silicone compound to the entire composition is preferably from about 0.1% to about 10% by weight. The silicone compounds hereof can include volatile soluble or insoluble, or nonvolatile soluble or insoluble silicone conditioning agents. By soluble what is meant is that the silicone compound is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone. The silicone compound herein is preferably made by conventional polymerization, and mechanically emulsified.

The silicone compounds for use herein will preferably have a viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from about 10,000 to about 1,800,000, and even more preferably from about 25,000 to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method CTM0004, July 20, 1970, which is incorporated by reference herein in its entirety. Silicone compound of high molecular weight may be made by emulsion polymerization.

Silicone compounds useful herein include polyalkyl polyaryl siloxanes, polyalkyleneoxide-modified siloxanes, silicone resins, amino-substituted siloxanes, and mixtures thereof. The silicone compound is preferably selected from the group consisting of polyalkyl polyaryl siloxanes, polyalkyleneoxide-modified siloxanes, silicone resins, and mixtures thereof, and more preferably from one or more polyalkyl polyaryl siloxanes.

Polyalkyl polyaryl siloxanes useful here in include those with the following structure (I)



wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl

groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy, methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone compounds are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone compounds are available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series. Polymethylphenylsiloxanes, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid, are useful herein.

Also preferred, for enhancing the shine characteristics of hair, are highly arylated silicone compounds, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone compounds are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

Another polyalkyl polyaryl siloxane that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone compounds. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are

General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference in their entirety. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Polyalkyleneoxide-modified siloxanes useful herein include, for example, polypropylene oxide modified and polyethylene oxide modified polydimethylsiloxane. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Silicone resins, which are highly crosslinked polymeric siloxane systems, are useful herein. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone

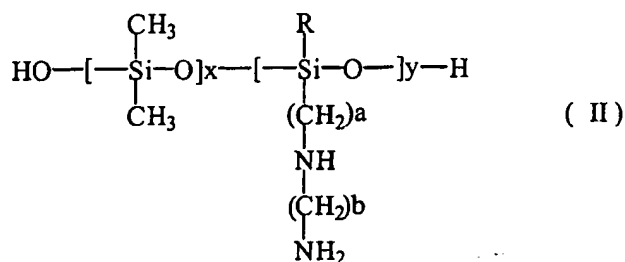
compounds on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the material given the CTFA designation polymethylsilsequioxane, which is commercially available as TospearlTM from Toshiba Silicones.

Silicone resins can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which make up the silicone. Briefly, the symbol M denotes the mono-functional unit $(\text{CH}_3)_3\text{SiO}_{1.5}$; D denotes the difunctional unit $(\text{CH}_3)_2\text{SiO}$; T denotes the trifunctional unit $(\text{CH}_3)\text{SiO}_{1.5}$; and Q denotes the quadri- or tetra-functional unit SiO_2 . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system. Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

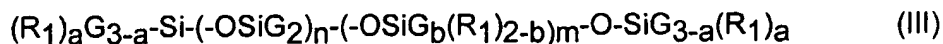
The silicone resins for use herein which are preferred are MQ, MT, MTQ, MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl. Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

Amino-substituted siloxanes useful herein include those represented by the following structure (II)

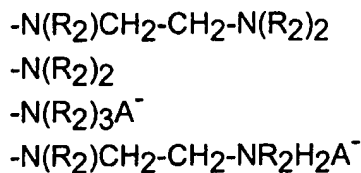


wherein R is CH₃ or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino-substituted siloxane fluids include those represented by the formula (III)

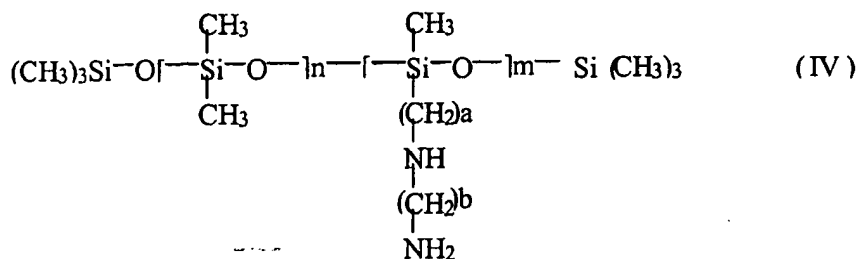


in which G is chosen from the group consisting of hydrogen, phenyl, OH, C₁-C₈ alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R₁ is a monovalent radical of formula C_qH_{2q}L in which q is an integer from 2 to 8 and L is chosen from the groups



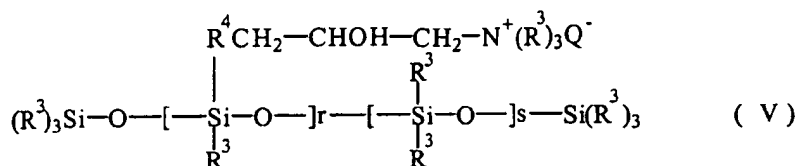
in which R₂ is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A⁻ denotes a halide ion.

An especially preferred amino-substituted siloxane corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



In this formula n and m are selected depending on the molecular weight of the compound desired.

- 5 Other amino-substituted siloxane which can be used are represented by the formula (V):



- 10 where R^3 denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R^4 denotes a hydrocarbon radical, preferably a $\text{C}_1 - \text{C}_{18}$ alkylene radical or a $\text{C}_1 - \text{C}_{18}$, and more preferably $\text{C}_1 - \text{C}_8$, alkyleneoxy radical; Q^- is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

AQUEOUS CARRIER

- 20 The composition of the present invention comprises an aqueous carrier. The level and species of the carrier are selected according to the compatibility with other components, and other desired characteristic of the product.

- The carrier useful in the present invention include water and water solutions of lower alkyl alcohols and polyhydric alcohols. The lower alkyl alcohol useful herein are monohydric alcohols having 1 to 6 carbons, more preferably ethanol and isopropanol. The polyhydric alcohols useful herein include propylene glycol, hexylene glycol, glycerin, and propane diol.

Preferably, the aqueous carrier is substantially water. Deionized water is preferably used. Water from natural sources including mineral cations can also

be used, depending on the desired characteristic of the product. Generally, the compositions of the present invention comprise from about 20% to about 95%, preferably from about 30% to about 92%, and more preferably from about 50% to about 90% water.

5 HIGH MELTING POINT FATTY COMPOUND

The composition of the present invention may further comprise a high melting point fatty compound. The high melting point fatty compound useful herein have a melting point of 25°C or higher, and is selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid
10 derivatives, and mixtures thereof. It is understood by the artisan that the compounds disclosed in this section of the specification can in some instances fall into more than one classification, e.g., some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for
15 convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than 25°C. Such compounds of low melting point are not intended to be included in this section. Nonlimiting
20 examples of the high melting point compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

These high melting point fatty compounds, together with the cationic conditioning agent, provide a gel network suitable for providing various
25 conditioning benefits such as slippery and slick feel on wet hair, and softness, moisturized feel, and fly-away control on dry hair.

The high melting point fatty compound is included in the composition at a level by weight of from about 0.1% to about 15%, preferably from about 0.5% to about 10%, more preferably from about 1% to about 7%.

30 The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols are saturated and can be straight or branched chain alcohols. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids are saturated and can be straight or branched chain acids. Also included are diacids, triacids, and other multiple acids which meet the requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid derivatives include materials such as methyl stearyl ether; the ceteth series of compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers of cetyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; the steareth series of compounds such as steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; cetareth 1 through cetareth-10, which are the ethylene glycol ethers of cetareth alcohol, *i.e.* a mixture of fatty alcohols containing predominantly cetyl and stearyl alcohol, wherein the numeric designation indicates the number of ethylene glycol moieties present; C₁-C₃₀ alkyl ethers of the ceteth, steareth, and cetareth compounds just described; polyoxyethylene ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl stearate, myristyl myristate, polyoxyethylene cetyl ether stearate, polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate, ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene distearate, propyleneglycol monostearate, propyleneglycol distearate, trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

High melting point fatty compounds of a single compound of high purity are preferred. Single compounds of pure fatty alcohols selected from the group of pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred.

By "pure" herein, what is meant is that the compound has a purity of at least

about 90%, preferably at least about 95%. These single compounds of high purity provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available high melting point fatty compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from Shin Nihon Rika (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy).

ADDITIONAL CONDITIONING AGENT

The composition of the present invention may contain an additional conditioning agent selected from the group consisting of a cationic polymer, a betaine conditioning agent, an amphoteric polymer, and mixtures thereof.

Cationic Polymer

The cationic polymer can be included in the composition at a level by weight of from about 0.1% to about 10%, preferably from about 0.25% to about 8%, more preferably from about 0.5% to about 3%. As used herein, the term "polymer" shall include materials whether made by polymerization of one type of monomer or made by two (i.e., copolymers) or more types of monomers.

Preferably, the cationic polymer is a water-soluble cationic polymer. By "water soluble" cationic polymer, what is meant is a polymer which is sufficiently soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. The preferred polymer will be sufficiently soluble to form a substantially clear solution at 0.5% concentration, more preferably at 1.0% concentration.

The cationic polymers hereof will generally have a weight average molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers will generally have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, and mixtures thereof.

The cationic charge density is preferably at least about 0.1 meq/gram, more preferably at least about 1.5 meq/gram, even more preferably at least

about 1.1 meq/gram, still more preferably at least about 1.2 meq/gram. Cationic charge density of the cationic polymer can be determined according to the Kjeldahl Method. Those skilled in the art will recognize that the charge density of amino-containing polymers may vary depending upon pH and the isoelectric point of the amino groups. The charge density should be within the above limits at the pH of intended use.

Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g., Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C₁ - C₇ alkyl groups, more preferably C₁ - C₃ alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the composition. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, and then optionally can be converted to ammonium by a quaternization reaction. Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by

reaction with a salt of the formula $R'X$ wherein R' is a short chain alkyl, preferably a $C_1 - C_7$ alkyl, more preferably a $C_1 - C_3$ alkyl, and X is an anion which forms a water soluble salt with the quaternized ammonium.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the $C_1 - C_3$ alkyls, more preferably C_1 and C_2 alkyls. Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably $C_1 - C_7$ hydrocarbyls, more preferably $C_1 - C_3$, alkyls.

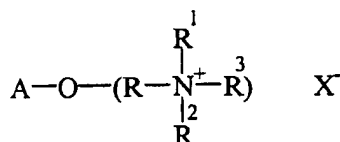
The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated

carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

5 Cationic polysaccharide polymer materials suitable for use herein include those of the-formula:



10 wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual, R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R¹, R², and R³ independently are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms
15 for each cationic moiety (i.e., the sum of carbon atoms in R¹, R² and R³) preferably being about 20 or less, and X is an anionic counterion, as previously described.

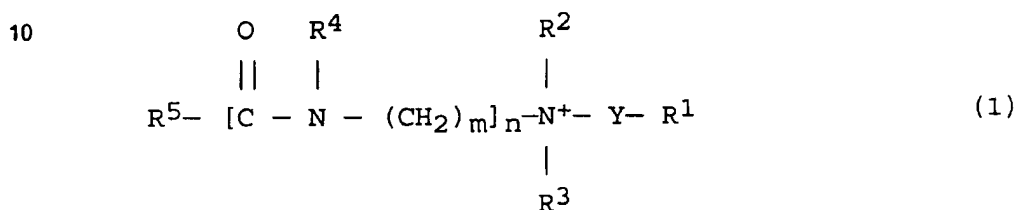
Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR® and LR® series of polymers, as salts of hydroxyethyl cellulose
20 reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp.
25 (Edison, NJ, USA) under the tradename Polymer LM-200®.

Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially available from Celanese Corp. in their Jaguar R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent
30 3,962,418, incorporated herein by reference), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated herein by reference.)

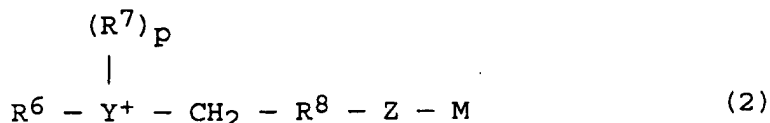
Betaine Conditioning Agent

Betaine conditioning agents useful herein are those which are capable of depositing on the hair and providing conditioning benefits. Although betaine conditioning agents herein may have some surfactant properties, they are generally too low to provide good cleaning properties. Betaine conditioning agents are preferably contained at a level of from about 0.2% to about 10%.

Betaine conditioning agents useful herein are those having general formulae (1) and (2), preferably (1):



wherein: R¹ is COOM or CH(OH)CH₂SO₃M, preferably COOM; R² and R³, independently, are hydrogen, alkyl of 1 to about 4 carbons, CH₂COOM, CH₂CH₂OH, CH₂CH₂OCH₂CH₂COOM, or (CH₂CH₂O)_xH wherein x is an integer from 1 to about 25, preferably methyl or ethyl; R⁴ is hydrogen or alkyl of 1 to about 4 carbons, preferably hydrogen; R⁵ is a straight or branched, saturated or unsaturated alkyl of about 16 to about 30 carbon atoms, preferably a straight saturated or unsaturated alkyl of about 16 to about 22 carbon atoms; Y is an alkyl of 1 to about 4 carbons, preferably methyl; m is an integer from 1 to about 7, preferably from 1 to about 4; n is 1 or 0; and M is hydrogen or an alkali metal, alkaline earth metal, or ammonium; and



wherein R⁶ is a saturated or unsaturated alkyl, alkenyl, or hydroxy alkyl of from about 16 to about 30 carbon atoms, preferably a saturated or unsaturated alkyl of about 16 to about 22 carbon atoms; Y is nitrogen, phosphorus or sulfur atom; R⁷ is an alkyl or monohydroxyalkyl group containing 1 to about 4 carbon atoms; p is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R⁸ is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms; Z is a

carboxylate, sulfonate, sulfate, phosphonate, or phosphate; and M is as previously defined.

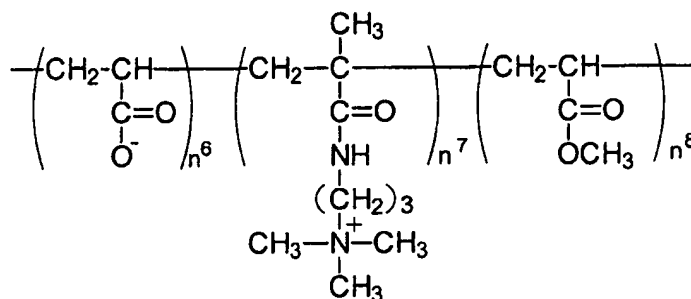
Examples of betaine conditioning agents useful herein include: alkylbetaines such as cetyldimethylcarboxymethylbetaine, 5 stearyldimethylcarboxymethylbetaine, isostearyldimethylcarboxymethylbetaine, behenyldimethylcarboxymethylbetaine, oleyldimethylcarboxymethylbetaine, stearyl-bis-(2-hydroxypropyl) carboxymethylbetaine, oleyldimethyl- γ -carboxypropylbetaine, and stearyldihydroxyethylbetaine; amido betaines such as cetylamidodimethylcarboxymethyl betaine, isostearamidopropyl betaine, 10 isostearylamidodimethylcarboxymethyl betaine, and stearylamidodimethylcarboxypropyl betaine; amidosulfobetaines such as stearylamidodimethylsulfopropylbetaine; sulfobetaines such as stearyldimethylsulfopropylbetaine; sultaines such as stearyldimethylpropylsultaine; and amidosultaines. Commercially available 15 material highly suitable for use herein include stearyl dimethyl betaine with tradename Rikabion A-700 available from New Japan Chemical, oleyl dimethyl betaine with tradename Rikabion A-300 available from New Japan Chemical, and stearyl dihydroxyethyl betaine with tradename Anon AB 202 available from Nihon Oil & Fats.

20 Amphoteric polymer

The amphoteric polymers useful herein are those which provide conditioning benefit to the hair. Although some of the amphoteric polymers herein may have some hair holding or hair fixative properties, such hair holding or hair fixative properties are not a requirement for the amphoteric polymers 25 herein. The amphoteric polymers useful herein are those including at least one cationic monomer and at least one anionic monomer; the cationic monomer being quaternary ammonium, preferably dialkyl diallyl ammonium chloride or carboxylamidoalkyl trialkyl ammonium chloride; and the anionic monomer being carboxylic acid. The amphoteric polymers herein may include nonionic 30 monomers such as acrylamine, methacrylate, or ethacrylate. Further, the amphoteric polymers useful herein do not contain betanized monomers. Amphoteric polymers are preferably contained at a level of from about 0.01% to about 5%.

Useful herein are polymers with the CTFA name Polyquaternium 22, 35 Polyquaternium 39, and Polyquaternium 47. Such polymers are, for example,

copolymers consisting of dimethyldiallyl ammonium chloride and acrylic acid, terpolymers consisting of dimethyldiallyl ammonium chloride and acrylamide, and terpolymers consisting of acrylic acid methacrylamidopropyl trimethylammonium chloride and methyl acrylate such as those of the following formula wherein the ratio of $n^6:n^7:n^8$ is 45:45:10:



Highly preferred is Polyquaternium 47. Highly preferred commercially available amphoteric polymers herein include Polyquaternium 22 with tradenames MERQUAT 280, MERQUAT 295, Polyquaternium 39 with tradenames MERQUAT PLUS 3330, MERQUAT PLUS 3331, and Polyquaternium 47 with tradenames MERQUAT 2001, MERQUAT 2001N, all available from Calgon Corporation.

Also useful herein are polymers resulting from the copolymerisation of a vinyl monomer carrying at least one carboxyl group, such as acrylic acid, methacrylic acid, maleic acid, itaconic acid, fumaric acid, crotonic acid, or alphachloroacrylic acid, and a basic monomer which is a substituted vinyl compound containing at least one basic nitrogen atom, such as dialkylaminoalkyl methacrylates and acrylates and dialkylaminoalkylmethacrylamides and acrylamides.

Also useful herein are polymers containing units derived from:

- i) at least one monomer chosen from amongst acrylamides or methacrylamides substituted on the nitrogen by an alkyl radical,
- ii) at least one acid comonomer containing one or more reactive carboxyl groups, and
- iii) at least one basic comonomer, such as esters, with primary, secondary and tertiary amine substituents and quaternary ammonium substituents, of acrylic and methacrylic acids, and the

product resulting from the quaternisation of dimethylaminoethyl methacrylate with dimethyl or diethyl sulfate.

The N-substituted acrylamides or methacrylamides which are most particularly preferred are the groups in which the alkyl radicals contain from 2 to 12 carbon atoms, especially N-ethylacrylamide, N-tert.-butylacrylamide, N-tert.-octylacrylamide, N-octylacrylamide, N-decylacrylamide and N-dodecylacrylamide and also the corresponding methacrylamides. The acid comonomers are chosen more particularly from amongst acrylic, methacrylic, crotonic, itaconic, maleic and fumaric acids and also the alkyl monoesters of maleic acid or fumaric acid in which alkyl has 1 to 4 carbon atoms.

The preferred basic comonomers are aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl and N-tert.-butylaminoethyl methacrylates.

Commercially available amphoteric polymers herein include octylacrylamine/acrylates/butylaminoethyl methacrylate copolymers with the tradenames AMPHOMER, AMPHOMER SH701, AMPHOMER 28-4910, AMPHOMER LV71, and AMPHOMER LV47 supplied by National Starch & Chemical.

LOW MELTING POINT OILS

The hair conditioning composition of the present invention may further comprise a low melting point oil, which has a melting point of less than 25°C, and is preferably included in the composition at a level by weight of from about 0.1% to about 10%, more preferably from about 0.25% to about 6%. The low melting point oil herein provides an improved rinse feel by eliminating the ease of rinsing difficulties. It is believed that the poly α -olefin oil reduces the slicky/slimy feel of other conditioning agents by imparting a draggy feel to the hair when the hair is rinsed. Low melting point oils useful herein include fatty alcohols and their derivatives, fatty acids and their derivatives, hydrocarbons, poly- α olefin oils, and high molecular weight ester oils. The additional oily compounds of this section are to be distinguished from the high melting point compounds described above. Nonlimiting examples of the additional oily compounds are found in International Cosmetic Ingredient Dictionary, Fifth Edition, 1993, and CTFA Cosmetic Ingredient Handbook, Second Edition, 1992.

The fatty alcohols useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty alcohols

can be straight or branched chain alcohols and are unsaturated alcohols, preferably unsaturated alcohols. Nonlimiting examples of these compounds include oleyl alcohol, palmitoleic alcohol, linoleyl alcohol, and recinoleyl alcohol.

The fatty acids useful herein include those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and are unsaturated. Suitable fatty acids include, for example, oleic acid, linoleic acid, linolenic acid, ethyl linolenic acid, ethyl linolenic acid, arachidonic acid, and ricinolic acid.

The fatty acid derivatives and fatty alcohol derivatives are defined herein to include, for example, esters of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of fatty alcohols, alkyl ethers of alkoxylated fatty alcohols, and bulky ester oils such as pentaerythritol ester oils, trimethylol ester oils, citrate ester oils, glyceryl ester oils, and mixtures thereof. Nonlimiting examples of fatty acid derivatives and fatty alcohol derivatives, include, for example, methyl linoleate, ethyl linoleate, isopropyl linoleate, isodecyl oleate, isopropyl oleate, ethyl oleate, octyldodecyl oleate, oleyl oleate, decyl oleate, butyl oleate, methyl oleate, octyldodecyl stearate, octyldodecyl isostearate, octyldodecyl isopalmitate, octyl isopelargonate, octyl pelargonate, hexyl isostearate, isopropyl isostearate, isodecyl isononanoate, isopropyl isostearate, ethyl isostearate, methyl isostearate and Oleth-2. Bulky ester oils such as pentaerythritol ester oils, trimethylol ester oils, citrate ester oils and glyceryl ester oils useful herein are those which have a molecular weight of less than about 800, preferably less than about 500.

The hydrocarbons useful herein include straight chain, cyclic, and branched chain hydrocarbons which can be either saturated or unsaturated, so long as they have a melting point of not more than about 25°C. These hydrocarbons have from about 12 to about 40 carbon atoms, preferably from about 12 to about 30 carbon atoms, and preferably from about 12 to about 22 carbon atoms. Also encompassed herein are polymeric hydrocarbons of alkenyl monomers, such as polymers of C_{2-6} alkenyl monomers. These polymers can be straight or branched chain polymers. The straight chain polymers will typically be relatively short in length, having a total number of carbon atoms as described above. The branched chain polymers can have substantially higher chain lengths. The number average molecular weight of such materials can vary

widely, but will typically be up to about 500, preferably from about 200 to about 400, and more preferably from about 300 to about 350. Also useful herein are the various grades of mineral oils. Mineral oils are liquid mixtures of hydrocarbons that are obtained from petroleum. Specific examples of suitable hydrocarbon materials include paraffin oil, mineral oil, dodecane, isododecane, hexadecane, isohexadecane, eicosene, isoeicosene, tridecane, tetradecane, polybutene, polyisobutene, and mixtures thereof.

Commercially available fatty alcohols and their derivatives useful herein include: oleyl alcohol with tradename UNJECOL 90BHR available from Shin Nihon Rika, various liquid esters with tradenames SCHERCEMOL series available from Scher, and hexyl isostearate with a tradename HIS and isopropyl isostearate having a tradename ZPIS available from Kokyu Alcohol. Commercially available bulky ester oils useful herein include: trimethylolpropane tricaprilate/tricaprate with tradename MOBIL ESTER P43 from Mobil Chemical Co. Commercially available hydrocarbons useful herein include isododecane, isohexadecane, and isoeicosene with tradenames PERMETHYL 99A, PERMETHYL 101A, and PERMETHYL 1082, available from Presperse (South Plainfield New Jersey, USA), a copolymer of isobutene and normal butene with tradenames INDOPOL H-100 available from Amoco Chemicals (Chicago Illinois, USA), mineral oil with tradename BENOL available from Witco, and isoparaffin with tradename ISOPAR from Exxon Chemical Co. (Houston Texas, USA).

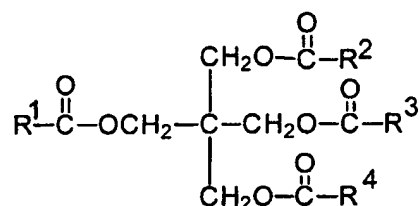
Poly α -olefin oils useful herein are those derived from 1-alkene monomers having from about 6 to about 16 carbons, preferably from about 6 to about 12 carbons atoms. Nonlimiting examples of 1-alkene monomers useful for preparing the poly α -olefin oils include 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, branched isomers such as 4-methyl-1-pentene, and mixtures thereof. Preferred 1-alkene monomers useful for preparing the poly α -olefin oils are 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and mixtures thereof. Poly α -olefin oils useful herein further have a viscosity of from about 1 to about 35,000 cst, a molecular weight of from about 200 to about 60,000, preferably less than 6,000, and more preferably 800; and a polydispersity of no more than about 3.

Particularly useful poly α -olefin oils herein include polydecenes with tradenames PURESYN 6 having a number average molecular weight of about 500, PURESYN 100 having a number average molecular weight of about 3000

and PURESYN 300 having a number average molecular weight of about 6000 available from Mobil Chemical Co.

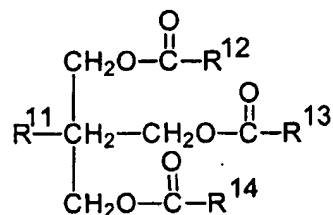
High molecular weight ester oils useful herein include pentaerythritol ester oils, trimethylol ester oils, citrate ester oils, glyceryl ester oils, and mixtures thereof. The high molecular weight ester oils herein are "water-insoluble". As used herein, the term "water-insoluble" means the compound is substantially not soluble in water at 25°C; when the compound is mixed with water at a concentration by weight of above 1.0%, preferably at above 0.5%, the compound is temporarily dispersed to form an unstable colloid in water, then is quickly separated from water into two phases.

Pentaerythritol ester oils useful herein are those having the following formula:



wherein R¹, R², R³, and R⁴, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R¹, R², R³, and R⁴, independently, are branched, straight, saturated, or unsaturated alkyl groups having from about 8 to about 22 carbons. More preferably, R¹, R², R³ and R⁴ are defined so that the molecular weight of the compound is from about 800 to about 1200.

Trimethylol ester oils useful herein are those having the following formula:

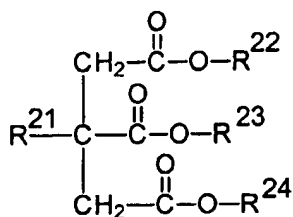


wherein R¹¹ is an alkyl group having from 1 to about 30 carbons, and R¹², R¹³, and R¹⁴, independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R¹¹ is ethyl and R¹², R¹³, and R¹⁴, independently, are branched, straight, saturated, or unsaturated alkyl groups having from 8 to about 22 carbons. More preferably,

R^{11} , R^{12} , R^{13} and R^{14} are defined so that the molecular weight of the compound is from about 800 to about 1200.

Particularly useful pentaerythritol ester oils and trimethylol ester oils herein include pentaerythritol tetraisostearate, pentaerythritol tetraoleate, trimethylolpropane triisostearate, trimethylolpropane trioleate, and mixtures thereof. Such compounds are available from Kokyo Alcohol with tradenames KAKPTI, KAKTTI, and Shin-nihon Rika with tradenames PTO, ENUJERUBU TP3SO.

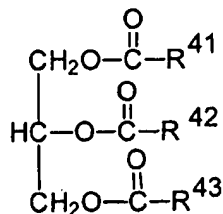
Citrate ester oils useful herein are those having a molecular weight of at least about 500 having the following formula:



wherein R^{21} is OH or CH_3COO , and R^{22} , R^{23} , and R^{24} , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons. Preferably, R^{21} is OH, and R^{22} , R^{23} , and R^{24} , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 8 to about 22 carbons. More preferably, R^{21} , R^{22} , R^{23} and R^{24} are defined so that the molecular weight of the compound is at least about 800.

Particularly useful citrate ester oils herein include triisocetyl citrate with tradename CITMOL 316 available from Bernel, triisostearyl citrate with tradename PELEMOL TISC available from Phoenix, and trioctyldodecyl citrate with tradename CITMOL 320 available from Bernel.

Glyceryl ester oils useful herein are those having a molecular weight of at least about 500 and having the following formula:



wherein R^{41} , R^{42} , and R^{43} , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 1 to about 30 carbons.

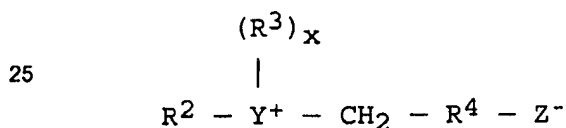
Preferably, R^{41} , R^{42} , and R^{43} , independently, are branched, straight, saturated, or unsaturated alkyl, aryl, and alkylaryl groups having from 8 to about 22 carbons. More preferably, R^{41} , R^{42} , and R^{43} are defined so that the molecular weight of the compound is at least about 800.

5 Particularly useful glyceryl ester oils herein include triisostearin with tradename SUN ESPOL G-318 available from Taiyo Kagaku, triolein with tradename CITHROL GTO available from Croda Surfactants Ltd., trilinolein with tradename EFADERMA-F available from Vevy, or tradename EFA-GLYCERIDES from Brooks.

10 AMPHOTERIC SURFACTANTS

Amphoteric surfactants useful herein include those called zwitterionic surfactants in the art. Amphoteric surfactants useful herein include the derivatives of aliphatic secondary and tertiary amines in which the aliphatic radical is straight or branched and one of the aliphatic substituents contains from
15 about 8 to about 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Amphoteric surfactants for use herein include the derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals are straight or branched, and wherein one of the aliphatic
20 substituents contains from about 8 to about 18 carbon atoms and one contains an anionic group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate. A general formula for these compounds is:

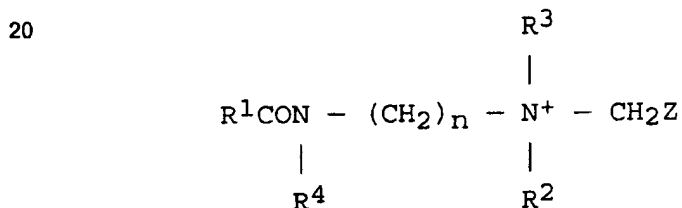


where R^2 contains an alkyl, alkenyl, or hydroxy alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties and from 0
30 to about 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^3 is an alkyl or monohydroxyalkyl group containing 1 to about 3 carbon atoms; X is 1 when Y is a sulfur atom, and 2 when Y is a nitrogen or phosphorus atom; R^4 is an alkylene or hydroxyalkylene of from 1 to about 4 carbon atoms and Z is a radical selected from the group consisting
35 of carboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples of amphoteric surfactants also include sultaines and amidosultaines. Sultaines, including amidosultaines, include for example, cocodimethylpropylsultaine, stearyldimethylpropylsultaine, lauryl-bis-(2-hydroxyethyl)propylsultaine and the like; and the amidosultaines such as cocamidodimethylpropylsultaine, stearylamidododimethylpropylsultaine, laurylamido-bis-(2-hydroxyethyl)propylsultaine, and the like. Preferred are amidohydroxysultaines such as the C₈-C₁₈ hydrocarbylamidopropylhydroxy sultaines, especially C₈-C₁₄ hydrocarbylamidopropylhydroxysultaines, e.g., laurylamidopropylhydroxysultaine and cocamidopropylhydroxysultaine. Other sultaines are described in U.S. Patent 3,950,417, which is incorporated herein by reference in its entirety.

Other suitable amphoteric surfactants are the aminoalkanoates of the formula RNH(CH₂)_nCOOM, the iminodialkanoates of the formula RN[(CH₂)_mCOOM]₂ and mixtures thereof; wherein n and m are numbers from 1 to about 4, R is C₈ - C₂₂ alkyl or alkenyl, and M is hydrogen, alkali metal, alkaline earth metal, ammonium or alkanolammonium.

Other suitable amphoteric surfactants include those represented by the formula :



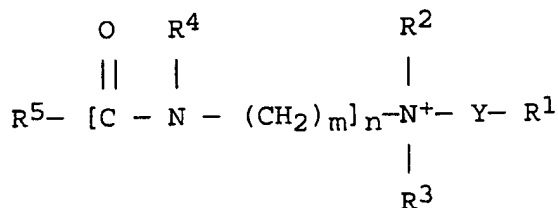
wherein R¹ is C₈ - C₂₂ alkyl or alkenyl, preferably C₈ - C₁₆, R² and R³ is independently selected from the group consisting of hydrogen, -CH₂CO₂M, -CH₂CH₂OH, -CH₂CH₂OCH₂CH₂COOM, or -(CH₂CH₂O)_mH wherein m is an integer from 1 to about 25, and R⁴ is hydrogen, -CH₂CH₂OH, or CH₂CH₂OCH₂CH₂COOM, Z is CO₂M or CH₂CO₂M, n is 2 or 3, preferably 2, M is hydrogen or a cation, such as alkali metal (e.g., lithium, sodium, potassium), alkaline earth metal (beryllium, magnesium, calcium, strontium, barium), or ammonium. This type of surfactant is sometimes classified as an imidazoline-type amphoteric surfactant, although it should be recognized that it does not necessarily have to be derived, directly or indirectly, through an imidazoline

intermediate. Suitable materials of this type are marketed under the tradename MIRANOL and are understood to comprise a complex mixture of species, and can exist in protonated and non-protonated species depending upon pH with respect to species that can have a hydrogen at R². All such variations and species are meant to be encompassed by the above formula.

Examples of surfactants of the above formula are monocarboxylates and di-carboxylates. Examples of these materials include cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate (alternately referred to as cocoamphodiacetate), and cocoamphoacetate.

Commercial amphoteric surfactants include those sold under the trade names MIRANOL C2M CONC. N.P., MIRANOL C2M CONC. O.P., MIRANOL C2M SF, MIRANOL CM SPECIAL (Miranol, Inc.); ALKATERIC 2CIB (Alkaril Chemicals); AMPHOTERGE W-2 (Lonza, Inc.); MONATERIC CDX-38, MONATERIC CSH-32 (Mona Industries); REWOTERIC AM-2C (Rewo Chemical Group); and SCHERCOTERIC MS-2 (Scher Chemicals).

Betaine surfactants suitable for use herein are those represented by the formula:



wherein: R¹ is a member selected from the group consisting of COOM and CH(OH)CH₂SO₃M

R² is lower alkyl or hydroxyalkyl; R³ is lower alkyl or hydroxyalkyl; R⁴ is a member selected from the group consisting of hydrogen and lower alkyl; R⁵ is higher alkyl or alkenyl; Y is lower alkyl, preferably methyl; m is an integer from 2 to 7, preferably from 2 to 3; n is the integer 1 or 0; M is hydrogen or a cation, as previously described, such as an alkali metal, alkaline earth metal, or ammonium. The term "lower alkyl" or "hydroxyalkyl" means straight or branch chained, saturated, aliphatic hydrocarbon radicals and substituted hydrocarbon radicals having from one to about three carbon atoms such as, for example, methyl, ethyl,

propyl, isopropyl, hydroxypropyl, hydroxyethyl, and the like. The term "higher alkyl or alkenyl" means straight or branch chained saturated (i.e., "higher alkyl") and unsaturated (i.e., "higher alkenyl") aliphatic hydrocarbon radicals having from about 8 to about 20 carbon atoms such as, for example, lauryl, cetyl, stearyl, oleyl, and the like. It should be understood that the term "higher alkyl or alkenyl" includes mixtures of radicals which may contain one or more intermediate linkages such as ether or polyether linkages or non-functional substituents such as hydroxyl or halogen radicals wherein the radical remains of hydrophobic character.

Examples of surfactant betaines of the above formula wherein n is zero which are useful herein include the alkylbetaines such as cocodimethylcarboxymethylbetaine, lauryldimethylcarboxymethylbetaine, lauryldimethyl- α -carboxyethylbetaine, cetyldimethylcarboxymethylbetaine, lauryl-bis-(2-hydroxyethyl)-carboxymethylbetaine, stearyl-bis-(2-hydroxypropyl)carboxymethylbetaine, oleyldimethyl- γ -carboxypropylbetaine, lauryl-bis-(2-hydroxypropyl)- α -carboxyethylbetaine, etc. The sulfobetaines may be represented by cocodimethylsulfopropylbetaine, stearyldimethylsulfopropylbetaine, lauryl-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

Specific examples of amido betaines and amidosulfobetaines useful herein include the amidocarboxybetaines, such as cocamidodimethylcarboxymethylbetaine, laurylamidodimethylcarboxymethylbetaine, cetylamidodimethylcarboxymethylbetaine, laurylamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, cocamido-bis-(2-hydroxyethyl)-carboxymethylbetaine, etc. The amidosulfobetaines may be represented by cocamidodimethylsulfopropylbetaine, stearylamidodimethylsulfopropylbetaine, laurylamido-bis-(2-hydroxyethyl)-sulfopropylbetaine, and the like.

ANTIDANDRUFF AGENT

The present composition may contain a safe and effective amount of an antidandruff agent. When present, the antidandruff agent is typically used at a level from about 0.1% to about 5%, preferably from about 0.3% to about 5% by weight of the composition.

Without being bound by theory, it is believed that the coacervate made by the polyhydrophilic anionic surfactants and cationic conditioning agents of the

present invention are also capable of trapping and effectively delivering the antidandruff agents herein to the hair surface.

Pyrithione salts are useful herein. Suitable pyrithione salts are heavy metal salts of 1-hydroxy-2-pyridinethione, the heavy metal salts being zinc, tin, cadmium, magnesium, aluminium, and zirconium. Preferred is zinc salt of 1-hydroxy-2-pyridinethione known in the art as zinc pyrithione, more preferably in a particle size of up to about 20 microns, still preferably from about 1 to about 10 microns. Commercially available pyrithione salts suitable herein include Zinc Pyrithione available from Olin.

Selenium sulfides are useful herein. Selenium sulfides herein include selenium disulfide, as well as Se_xS_y in cyclic structure, wherein x and y are integers and $x + y$ equals 8. Preferred selenium sulfides are those having a particle size of less than about 15 microns, more preferably less than about 10 microns; wherein the particle size is measured by a laser light scattering device such as Malvern 3600 instrument.

Sulfur and octopirox, its salts, and its derivatives are also useful herein.

Antidandruff agents as mentioned above can be used alone, or in combination with one another.

ADDITIONAL COMPONENTS

The composition of the present invention may include other additional components, which may be selected by the artisan according to the desired characteristics of the final product and which are suitable for rendering the composition more cosmetically or aesthetically acceptable or to provide them with additional usage benefits. Such other additional components generally are used individually at levels of from about 0.001% to about 10%, preferably up to about 5% by weight of the composition.

A wide variety of other additional components can be formulated into the present compositions. These include: other conditioning agents such as hydrolysed collagen with tradename Peptin 2000 available from Hormel, vitamin E with tradename Emix-d available from Eisai, panthenol available from Roche, panthenyl ethyl ether available from Roche, a mixture of Polysorbate 60 and Cetearyl Alcohol with tradename Polawax NF available from Croda Chemicals, glycerylmonostearate available from Stepan Chemicals, coconut fatty acid monoethanolamide from Nippon Oil & Fats, hydroxyethyl cellulose available from Aqualon, hydrolysed keratin, proteins, plant extracts, and nutrients; hair-fixative

polymers such as amphoteric fixative polymers, cationic fixative polymers, anionic fixative polymers, nonionic fixative polymers, and silicone grafted copolymers; preservatives such as benzyl alcohol, methyl paraben, propyl paraben and imidazolidinyl urea; pH adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric acid, sodium hydroxide, sodium carbonate; suspending agents such as ethylene glycol distearate from Goldschmidt, viscosity modifying agents such as ammonium xylene sulfonate from Stepan Chemicals, potassium acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate and persulfate salts; hair reducing agents such as the thioglycolates; perfumes; and sequestering agents, such as disodium ethylenediamine tetra-acetate; ultraviolet and infrared screening and absorbing agents such as octyl salicylate, antidandruff agents such as zinc pyridinethione; and optical brighteners, for example polystyrylstilbenes, triazinstilbenes, hydroxycoumarins, aminocoumarins, triazoles, pyrazolines, oxazoles, pyrenes, porphyrins, imidazoles, and mixtures thereof.

EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

Examples 1 through 12 are conditioning shampoo compositions of the present invention which are particularly useful for rinse-off use.

COMPOSITIONS OF EXAMPLES 1-6

Components	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Ammonium Laureth-3 Sulfate	15	15	15	15	15	15
Ammonium lauryl sulfate	5	5	5	5	5	5
Silicone Emulsion-1 *1			0.50			
Silicone Emulsion-2 *2	0.46	0.46		0.10	2.0	0.46
Cocamidopropylbetaine *3		2				2
Puresyn 6*4		0.4	0.20			0.1
Stearyl Betaine *5		0.1	0.05			

Oleyl Betaine *6			0.05			
Polyquaterium-47 *7		0.10				
Cetyl Alcohol	0.42	0.42	0.42	0.42	0.42	0.42
Stearyl alcohol	0.18	0.18	0.18	0.18	0.18	0.18
Zinc Pyrithione *8		1.0				1.0
Ammonium xylene sulfonate	0.83	0.83	0.83	0.83	0.83	0.83
Cocamide MEA	0.87	0.87	0.87	0.87	0.87	0.87
Ethylene Glycol Distearate	2.0	2.0	2.0	2.0	2.0	2.0
Perfume solution	0.5	0.5	0.5	0.5	0.5	0.5
Kathon CG	0.05	0.05	0.05	0.05	0.05	0.05
Citric acid	0.04	0.04	0.04	0.04	0.04	0.04
Sodium Citrate dihydrate	0.45	0.45	0.45	0.45	0.45	0.45
Disodium EDTA	0.09	0.09	0.09	0.09	0.09	0.09
d- delta Tocopherol	0.1		0.1	0.1	0.1	0.1
Tocopherol acetate		0.02				
Panthenol*9	0.05	0.05	0.05	0.05	0.05	0.05
Panthenyl Ethyl Ether *10	0.05	0.05	0.05	0.05	0.05	0.05
Sodium sulfite		0.01				
Parsol MCX *11		0.02				
Benzophenone *12	0.01	0.01	0.01	0.01	0.01	0.01
Hydrolyzed Collagen *13	0.01	0.01	0.01	0.01	0.01	0.01
NaCl	4.00	4.00	4.00	4.00	4.00	4.00
Deionized Water	-----q.s. to 100%-----					

COMPOSITIONS OF EXAMPLES 7-12

Components	Ex. 7	Ex. 8	Ex. 9	Ex 10	Ex 11	Ex.12
Ammonium Laureth-3 Sulfate	10	10	10	10	10	10
Ammonium lauryl sulfate	6	6	6	6	6	2
Silicone Emulsion-1 *1						0.50
Silicone Emulsion-2 *2	0.50	0.50	0.50	0.20	1.50	
Cetyl alcohol	0.90	0.90	0.90	0.90	0.90	0.90
Polyquaterium-47 *7						0.2
Polyquaterium-10 *14	0.5	0.5	0.5	0.5	0.5	0.5
Puresyn 6 *4	0.4	0.4	0.4	0.4	0.4	0.25
Mobil P43 ester *15	0.10	0.10	0.10	0.10	0.10	

Cocamidopropylbetaine *3			2.0			1.0
Stearyl Betaine *5		0.20	0.20			0.1
Stearyl Dihydroxyethyl Betaine *16						0.1
Zinc Pyrithione *8						1.0
Cocamide MEA	0.80	0.80	0.80	0.80	0.80	1.5
Ethylene Glycol Distearate	1.5	1.5	1.5	1.5	1.5	1.5
Perfume solution	0.5	0.5	0.5	0.5	0.5	0.5
DMDM Hydantoin						0.37
Kathon CG	0.04	0.04	0.04	0.04	0.04	
Hydrolyzed Collagen *13	0.01	0.01	0.01	0.01	0.01	
Vitamin E *17	0.01			0.01	0.01	0.01
Panthenol *9	0.05	0.05	0.05	0.05	0.05	0.025
Panthenyl Ethyl Ether *10	0.05	0.05	0.05	0.05	0.05	0.025
Tocopherol acetate	0.05	0.01	0.01	0.05	0.05	0.2
Sodium sulfite	0.05	0.05	0.05	0.05	0.05	0.1
Parsol MCX *11	0.1	0.1	0.1	0.1	0.1	0.5
Benzophenone *12	0.2	0.2	0.2	0.2	0.2	0.2
Deionized Water	q.s. to 100%					

DEFINITIONS OF COMPONENTS

- *1 Silicone Emulsion-1: mechanically emulsified emulsion containing made using 16.2% polydimethylsiloxane having about 900 repeating units, 43.8% polydimethylsiloxane having about 100 repeating units, and 3.0% stearyl trimonium chloride, wherein the silicone compound has a particle size of about 250nm and the viscosity of the emulsion is approximately 60000 cPs available from Dow Corning Silicone
- *2 Silicone Emulsion-2: mechanically emulsified emulsion containing made using 14.85% polydimethylsiloxane having about 900 repeating units, 40.15% polydimethylsiloxane having about 100 repeating units, and 6.0% stearyltrimonium chloride, wherein the silicone compound has a particle size of about 250nm and the viscosity of the emulsion is approximately 60000 cPs available from Dow Corning Silicone
- *3 Cocamidopropylbetaine: Tego Betaine F available from TH Goldschmidt
- *4 Puresyn 6: polydecene having a molecular weight of about 500 available from Mobil Chemical Co.

- *5 Stearyl Betaine: Rikabion A-700 available from New Japan Chemical
- *6 Oleyl Betaine: Rikabion A-300 available from New Japan Chemical
- *7 Polyquaterium-47: Merquat 2001 available from Calgon
- *8 Zinc Pyrithione: available from Olin
- 5 *9 Panthenol: available from Roche
- *10 Panthenyl Ethyl-Ether: available from Roche
- *11 Parsol MCX: octyl methoxycinnamate available from Givaudan Roure
- *12 Benzophenone: available from Rhone Poulenc
- *13 Hydrolyzed Collagen: Peptin 2000 available from Hormel
- 10 *14 Polyquaterium-10: UCare Polymer JR400 available from Amerchol
- *15 Mobil P43 ester: trimethylolpropane tricaprilate/tricaprate available from Mobil Chemical Co.
- *16 Stearyl Dihydroxyethyl Betaine: Anon AB 202 available from Nihon Oil & Fats
- 15 *17 Vitamin E: Emix-d available from Roche

METHOD OF PREPARATION

The shampoo compositions of Examples 1 through 12 as shown above can be prepared by any conventional method well known in the art. Suitable methods are described below.

- 20 Surfactants and polymers, if present, are dispersed in water above 70°C and below 80°C to form a homogenous mixture. To this mixture are added the other ingredients except for the cationic silicone emulsion, perfume, and salt; the obtained mixture is agitated. The obtained mixture is then passed through a heat exchanger to cool to about 30°C, and then pumped through a high shear mill.
- 25 Then the cationic silicone emulsion, perfume, and salt are added. The obtained compositions are poured into bottles to make hair shampoo compositions.

- The embodiments disclosed and represented by the previous examples provide a colloidal coacervate by diluting each composition by about 10 folds, and the colloidal coacervates have an average particle size of less than about 30
- 30 microns.

The embodiments disclosed and represented by the previous examples have many advantages. For example, they can provide improved hair volume and conditioning benefit when the hair is dried such as prevention of fly away, ease of combing.

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

WHAT IS CLAIMED IS:

1. A conditioning shampoo composition comprising by weight:
 - (a) from about 0.05% to about 50% of an anionic surfactant wherein the anionic surfactant is substantially a monohydric anionic surfactant;
 - 5 (b) from about 0.05% to about 20% of a cationic silicone emulsion comprising, by weight of the cationic silicone emulsion, from about 2% to about 20% of a cationic surfactant; and an emulsifiable amount of a mechanically emulsified silicone compound having a particle size of from about 0.2 microns to about 2.5 microns; and
 - 10 (c) an aqueous carrier;wherein a colloidal coacervate is made by diluting the composition with water by about 10 folds, the colloidal coacervate having an average particle size of less than about 30 microns.
2. The conditioning shampoo composition according to Claim 1 wherein the cationic silicone emulsion comprises by weight from about 2% to about 8% of the cationic surfactant.
3. The conditioning shampoo composition according to Claim 1 or 2 further comprising a high melting point compound.
4. The conditioning shampoo composition according to Claim 3 further comprising an additional conditioning agent selected from the group consisting of a cationic polymer, a betaine conditioning agent, an amphoteric polymer, and mixtures thereof.
5. The conditioning shampoo composition according to Claim 3 further comprising a low melting point oil.
6. The conditioning shampoo composition according to Claim 3 further comprising an amphoteric surfactant.
7. The conditioning shampoo composition according to Claim 3 further comprising an antidandruff agent.

8. A method of increasing hair volume by applying the conditioning shampoo composition according to any of the preceding claims to the hair.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 99/28511

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 578 298 A (M. BERTHIAUME ET AL.) 26 November 1996 (1996-11-26) claims 1,16; examples 40,41	1
X	US 4 673 568 A (J. GROLLIER ET AL.) 16 June 1987 (1987-06-16) examples 8,10	1
X	EP 0 514 934 A (DOW CORNING CORP.) 25 November 1992 (1992-11-25) claim 1; examples II.16,,II.17,II.20	1
X	EP 0 674 898 A (UNILEVER PLC) 4 October 1995 (1995-10-04) claim 1; example I.A	1
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

27 September 2000

Date of mailing of the international search report

10/10/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Glikman, J-F

INTERNATIONAL SEARCH REPORT

Invention No.

PCT/US 99/28511

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 990 059 A (C. FINEL ET AL.) 23 November 1999 (1999-11-23) claim 1	1
A	US 4 733 677 A (R. GEE ET AL.) 29 March 1988 (1988-03-29) column 8, line 60 -column 9, line 5	1
A	EP 0 798 332 A (SHIN-ETSU CHEM. CO., LTD) 1 October 1997 (1997-10-01) column 1, line 1 -column 2, line 5; claim 1; examples 6,7	1
A	WO 98 19655 A (THE PROCTER & GAMBLE CO.) 14 May 1998 (1998-05-14) examples 1-3	1
A	D. HALLORAN ET AL.: "Organofunctional silicone microemulsions for hair formulations" COSMETICS AND TOILETRIES, vol. 113, no. 6, 1998, pages 61-64, XP000949886 the whole document	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. Classification No

PCT/US 99/28511

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5578298 A	26-11-1996	US 5683625 A DE 19518449 A FR 2720401 A GB 2289686 A, B JP 8059994 A	04-11-1997 30-11-1995 01-12-1995 29-11-1995 05-03-1996
US 4673568 A	16-06-1987	LU 85303 A BE 901410 A CA 1221912 A CH 662504 A DE 3447621 A FR 2562794 A GB 2157168 A, B IT 1208797 B JP 60224611 A NL 8403957 A	27-11-1985 28-06-1985 19-05-1987 15-10-1987 17-10-1985 18-10-1985 23-10-1985 10-07-1989 09-11-1985 01-11-1985
EP 514934 A	25-11-1992	BR 9201938 A CA 2068124 A DE 69209716 D DE 69209716 T JP 5139941 A MX 9202436 A	12-01-1993 25-11-1992 15-05-1996 12-09-1996 08-06-1993 01-11-1992
EP 674898 A	04-10-1995	BR 9501289 A CA 2145474 A JP 2955203 B JP 7277931 A	31-10-1995 01-10-1995 04-10-1999 24-10-1995
US 5990059 A	23-11-1999	AU 4623997 A BR 9712101 A CN 1237893 A WO 9813011 A EP 0952810 A JP 2000507606 T	17-04-1998 31-08-1999 08-12-1999 02-04-1998 03-11-1999 20-06-2000
US 4733677 A	29-03-1988	CA 1302282 A DE 3774845 A EP 0270249 A JP 1914018 C JP 4078607 B JP 63130517 A	02-06-1992 09-01-1992 08-06-1988 23-03-1995 11-12-1992 02-06-1988
EP 798332 A	01-10-1997	JP 9316331 A US 5788884 A	09-12-1997 04-08-1998
WO 9819655 A	14-05-1998	AU 7666996 A BR 9612766 A EP 0946131 A JP 11500461 T	29-05-1998 07-12-1999 06-10-1999 12-01-1999